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Contemporary carbon fluxes do not reflect the long-term carbon balance of an Atlantic blanket bog

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Abstract

Peatlands are one of the largest terrestrial stores of carbon. Carbon exchange in peatlands is often assessed solely by measurement of contemporary fluxes; however, these fluxes frequently indicate a much stronger sink strength than that measured by the rate of C accumulation in the peat profile over longer timescales. Here we compare profile-based measurements of C accumulation with the published net ecosystem C balance for the largest peatland area in Britain, the Flow Country of northern Scotland. We estimate the long-term rate of C accumulation to be $15.4 \text{ g C m}^{-2} \text{ yr}^{-1}$ for a site where a recent eddy covariance study has suggested contemporary C uptake more than six times greater ($99.37 \text{ g C m}^{-2} \text{ yr}^{-1}$). Our estimate is supported by two further long-term C accumulation records from nearby sites which give comparable results. We demonstrate that a strong contemporary C sink strength may not equate to a strong long-term sink and explore reasons for this disparity. We recommend that contemporary C sequestration should be viewed in the context of the long-term ecological drivers, such as fires, ecohydrological feedbacks and the changing quality of litter inputs.

Introduction

Peatlands store more carbon (C) in a given area than any other terrestrial biome (Dise and Phoenix, 2011). They cover only 2–3% of the global land area but are estimated to store 612 GtC (Yu, 2011); equivalent to greater than half the CO₂ currently stored in the atmosphere (Dise, 2009). On a global scale, peatlands have been a persistent sink for atmospheric CO₂ throughout the Holocene (Yu, 2011), resulting in a net climatic cooling effect for all but the first few centuries of their initiation (Frolking and Roulet, 2007).

Peatlands are unusual in that they can store C over geological timescales, yet this C is located close to the surface and is vulnerable to climatic and anthropogenic disturbances (Frolking et al., 2011). Globally, degraded peatlands are thought to be emitting more than 1400 Mt tonnes of CO₂ annually (Joosten, 2009), more than international aviation and marine transport combined (Cames et al., 2015). In Scotland, our study area, degraded peatlands could be responsible for as much as 15% of national greenhouse gas emissions (Smith et al., 2009), and it is estimated that restoration of peatlands could provide up to 2.7 Mt CO₂-eq savings per year (Chapman et al., 2012). The capacity of restored peatlands to halt losses and to store and sequester C in the future has been recognised as a key criterion for prioritising areas for restoration (Artz et al., 2013, 2014). However, for many peatlands, there are no reliable baseline C accumulation rates against which to assess losses and gains. These uncertainties are even more acute at

the regional scale, and for certain peatland types such as blanket bogs (Lindsay, 2010). As a consequence, peatland C is rarely included in global climate models, despite the potential for strong climatic feedbacks (Limpens et al., 2008).

The two most widely used approaches to assessing C sequestration in peatlands involve measuring contemporary C fluxes to quantify the net ecosystem C budget (NECB) and determining the C accumulated over time in peat profiles. Flux studies focus on quantifying the key inputs and outputs of C from the system. Studies typically involve chamber or eddy covariance (EC) measurements of net CO₂ and CH₄ emission or uptake, combined with measurements of aquatic C fluxes. Such studies have the advantage of quantifying the different components of the C budget, with their differing greenhouse warming potentials. EC towers allow the recording of fluxes from a relatively large footprint but have the important disadvantage of being highly resource-intensive. Therefore, such records are relatively rare, only span the recent past, and frequently omit some elements of the C budget such as methane and aquatic C. The longest published flux record for any peatland, the Canadian raised bog Mer Bleue, only spans the last 15 years (Humphreys et al., 2014), and Auchencorth Moss, the longest record in the United Kingdom, only covers 11 years (Helfter et al., 2015).

To place these relatively short-term NECB records into their long-term context, it is necessary to consider the long-term accumulation of C in peatlands. Carbon accumulation studies combine analyses of the C content of the peat with a chronology of peat accumulation to quantify how much C a peatland has accumulated over time. Such studies have the advantage of longer temporal reach, but there are also disadvantages, in that they cannot distinguish among C fluxes and can only assess the C which is accumulated by the peatland and retained in the peat. As such, net loss of C will always appear as a slowdown in accumulation or a hiatus in peat growth; negative values are not possible. The latter is an important caveat, as factors such as fire or drought may cause peatlands to abruptly lose C which had previously been retained for hundreds of years (Frolking et al., 2014). Contemporary and palaeo C flux/sequestration methods are seldom used in combination (Roulet et al., 2007), and when they are, they have not been in agreement (Table 1).

Table 1. Sites with available long-term and contemporary rates of C accumulation. Sites which do not have multiple years of eddy covariance data and those with only long-term or contemporary measurements have been excluded. Contemporary C accumulation rates are listed as approximate for those sites where the carbon balance is missing either DOC or CH₄. Estimated error is included when available in the original publication.

Site	Fluxes included In contemporary carbon balance	Contemporary carbon balance in g C m ⁻² yr ⁻¹	Long term carbon accumulation in g C m ⁻² yr ⁻¹	References
Mer Bleue, Canada	CO ₂ , CH ₄ , DOC,	32 ± 40.0	18	(Roulet et al., 2016, 2007)
‘Wesern peatland’ Lac la Biche, Canada	CO ₂	~189 ± 47	21.5	(Flanagan and Syed, 2011)
Moanatuatua, New Zealand	CO ₂	~234	34.2	(Campbell et al., 2014; Schipper et al., 2002)
Forsinard/Cross Lochs, Scotland	CO ₂ , CH ₄ , DOC	99.4 ± 9.5	15.4 ± 5.1	(Levy and Gray, 2015); this publication
Moor House, Pennines, England	CO ₂ , DOC, POC, CH ₄	134.3 ± 32	27	(Garnett, 1998; Lloyd, 2010)
Lac Le Caron, Canada	CO ₂	~76	22.6	(Strachan et al., 2016; van Bellen et al., 2011)

While C accumulation profiles are globally quite numerous (Charman et al., 2013; Korhola et al., 2010; Turunen and Turunen, 2003; Van Bellen et al., 2011; Yu, 2006a, 2011), they are relatively rare in some otherwise well-studied regions such as the United Kingdom (Lindsay, 2010). Many published profile records have been dated at low resolution, sometimes with only a single dating point (Lindsay, 2010). Without a robust chronology, profile studies

reveal relatively little about the processes driving C dynamics. In Scotland, three published high-resolution (with four or more evenly spaced dates) C accumulation profiles are available, which span the entire period of bog development (Anderson, 2002). Several short profiles do exist for other sites (Billett et al., 2010; Yang et al., 2001), but these have mostly been for the relatively undecomposed acrotelm peat close to the surface, and as such are not representative of either long-term relative C accumulation (LORCA) or indeed the contemporary NECB which includes C exchange across the whole profile, not just the acrotelm.

Theoretically, measurements of NECB and LORCA should converge as NECB is measured over longer timescales (Frolking et al., 2014; Frolking and Roulet, 2007; Yu, 2012), yet the timescale over which this will occur is relatively unknown (Yu, 2012). A convergence of rates was seemingly apparent in the long record from Mer Bleue (Roulet et al., 2007); however, recent updates to the NECB record now suggest a contemporary C sequestration rate more than double that implied by peat cores (Roulet et al., 2016).

A six year EC record of C exchange has recently been published for a site in the Flow Country of Scotland, Cross Lochs (Levy and Gray, 2015), making it the third longest published record for C flux over Atlantic blanket bog (Artz et al., 2015) and arguably the only published EC record from a near pristine site (Levy and Gray, 2015). Incorporated in the C balance are measurements of CO₂, CH₄ and dissolved organic carbon (DOC). Non-CO₂ losses of C accounted for 13% of the total NECB and were mainly through DOC export. The site was presented as a strong and consistent sink for C over the 6 years, with a reported average NECB of $-99.37 \text{ g C m}^{-2} \text{ yr}^{-1}$. Using either the contemporary flux or the profile approach in isolation provides an incomplete picture of the processes driving C dynamics. In this study, we produced three C accumulation profiles to complement C exchange measurements for the Flow Country of Caithness and Sutherland. We then used a detailed chronology to assess whether the contemporary NECB at the Cross Lochs EC site is representative of long-term C accumulation. Finally, we discuss the factors driving C exchange over different timescales.

Site description

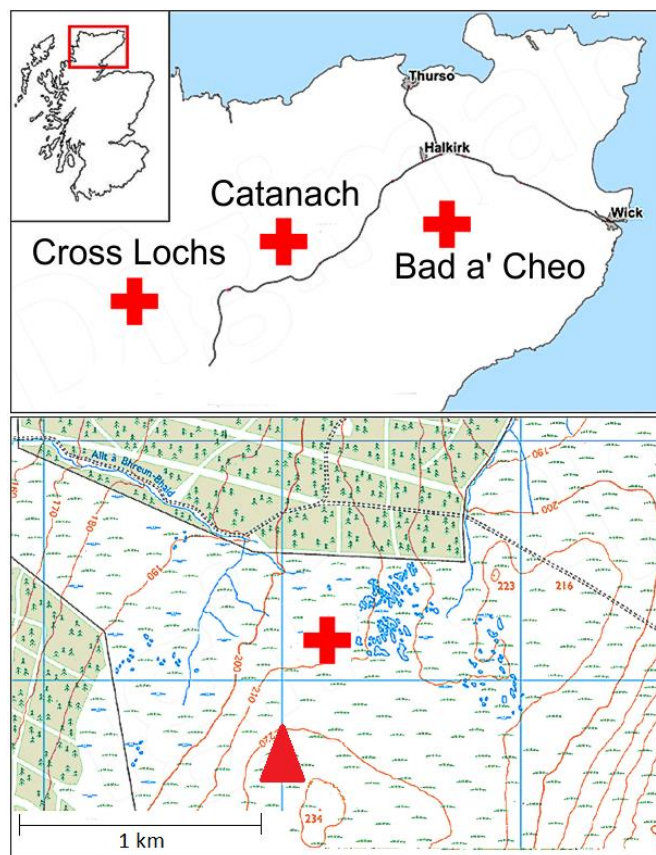


Figure 1. (a) Map of site locations in the north of Scotland marked by crosses and (b) detailed location of the Cross Lochs core, marked by a cross, and the eddy covariance tower, marked as a triangle. © Crown Copyright and Database Right 2016 Ordnance Survey (Digimap Licence).

We collected and dated cores from three sites in the Flow Country peatlands of Caithness and Sutherland (Figure 1). Our key site was Cross Lochs (OS National Grid reference: NC 85095 44154), which is the site of the EC tower considered by Levy and Grey (2015). This site is located within the RSPB Forsinard Flows National Nature Reserve, north-west of one of the pool systems which are characteristic of the Flow Country (Lindsay et al., 1988). The coring site was on a gentle slope, with a peat depth of 3.68 m and vegetation dominated by *Sphagnum* spp. (including *S. cuspidatum*, *S. papillosum* and *S. fallax*), *Calluna vulgaris*, *Trichophorum germanicum* and *Eriophorum angustifolium*. The peat was dominated by *Sphagnum* spp. and sedge remains with birch macrofossils towards the base. Humification varied downcore below the acrotelm alternating between H4 and H8 on the von Post scale. To assess the variability of LORCA across the Flow Country blanket bogs, we also sampled two other sites further to the east. Catanach (OS National Grid reference: ND 00605 48769) is also located within the RSPB Forsinard Flows National Nature Reserve, approximately 16 km north-east of Cross Lochs. The vegetation community was similar to Cross Lochs, including *Sphagnum* spp., along with *C. vulgaris*, *Betula nana* and *Arctostaphylos uva-ursi*; the peat was shallower (1.76 m), and the stratigraphy showed a mixture of *Sphagnum* and sedge peat which was more humified than at the other sites, typically H7 or above in the catotelm peat. Bad a' Cheo (OS National Grid reference: ND 16500 50174) is the easternmost sampling site, located in an area close to the A9 road which has been enclosed from grazing, except by deer, since 1968. The vegetation is dominated by *Sphagnum* spp., with *Calluna vulgaris* and *Eriophorum* spp. present, but less abundant than in the other sites. The peat depth at this site was 4.46 m. *Sphagnum* spp. remains were more abundant in the core stratigraphy compared with the previous sites; however, layers of sedge peat were also present. Birch wood was found in the bottom section of the core and humification was low, H4–H6, in the catotelm peat, and the vegetation composition was discernible even close to the base of the core.

Methods

Coring strategy

Cores were taken in October 2013 using a 7-cm-diameter, 1-m-long Russian peat corer (Belokopytov and Beresnevich, 1955 in Jowsey, 1966). Sampling was carried out from the midpoint between hummock and hollow microforms down to the mineral substrate, using the twin borehole method with 10 cm overlaps in order to minimise the risk of core compression, as outlined by De Vleeschouwer et al. (2010). The two boreholes were no more than 0.3 m apart. In the Cross Lochs site, the coring point was selected to be towards the centre of the EC tower footprint. Cores were transported and stored horizontally to avoid compression and refrigerated until analysis.

Bulk density, loss on ignition and carbon content analysis

Bulk density (ρ) measurements were carried out at 1 cm resolution for the Cross Lochs core and at 5 cm resolution for the other cores. Only a single sample was analysed for the uppermost 5 cm of the Cross Lochs core because of the fibrous nature of the peat. Sample volume was determined using the water displacement method (Chambers et al., 2011). Wet peat samples, approximately 10–20 cm³ in size, were carefully removed from the cores and placed into a volumetric cylinder and water volume displaced recorded. Samples were dried overnight at 105°C, and ground sub-samples incinerated at 550°C for 4 hours. The difference in weight before and after incineration was used to calculate loss on ignition.

C and N content was determined using an elemental analyser (Carol Erba 1108, University of Stirling), calibrated for each run using rice flour standards with standard checks every 10–12 samples. Loss on ignition and C content were measured at 5 cm resolution, and values for a small number of missing segments (for instance, because of low sample size in low-density peat) were interpolated.

Tephrochronology

Cryptotephrochronology offers the potential for high-precision dating, but at the expense of the time-consuming process of locating tephra shards (Gehrels et al., 2008). However, advances in multi-sensor core scanning offer the opportunity to speed up this process. The use of an 'ITRAX' scanner, which combines x-ray fluorescence (XRF) and x-radiography, has been shown to be effective for locating cryptotephra in lake sediments (Kylander et al., 2011). The

x-radiography has previously shown good potential for locating larger cryptotephra layers in the north of Scotland (Dugmore and Newton, 1992).

Multi-sensor core scanning was carried out using the ITRAX core scanner (Cox Analytical Systems) at the University of Aberystwyth. High-resolution (0.2 mm) x-radiographs were produced for all cores. XRF elemental profiles were produced at 0.2 mm resolution for Cross Lochs and 2 mm for the other sites. Tephra layers were identified by (1) visible black bands in the x-radiographs; (2) peaks in key elements such as Fe, Ca, Ti and Mn in the XRF-profiles; and (3) distinct troughs in the loss on ignition data. Where at least one of these features was apparent, 1-cm-thick samples spanning the zone of interest were sub-sampled. Samples were incinerated in a muffle furnace at 550°C for 4 hours; when necessary, they were soaked in 10% HCl to remove colouration from the ash and mounted on a slide for analysis as described by Pilcher and Hall (1992). These samples were examined microscopically at 400× magnification and tephra shards identified by their distinctive morphology.

A total of four tephra layers were found which contained quantities of shards sufficient for geochemical analysis. In order to link these tephra deposits to eruptions of known age, they were geochemically analysed by electron probe microanalysis (EPMA). Peat samples containing tephra from the relevant horizons were acid digested following Dugmore et al. (1992), and thin sections were prepared by mounting the shards in resin, grinding to a thickness of 75 µm and polishing until smooth using 6 and 1 µm diamond pastes (Dugmore et al., 1995).

Shards were analysed using Wavelength Dispersive Spectrometry (WDS) on a Cameca SX100 electron microprobe at the School of Geosciences, University of Edinburgh (see Supplementary Data, available online). The microprobe was set to an accelerating voltage of 15 kV, with a beam current of 2 nA (Na, Mg, Al, Si, Ca, Fe and K) and 80 nA (Ti, Mn and P). A beam diameter of 5 µm was used to prevent mobilisation of sodium. Standards of basaltic (USGS BCR2g) and rhyolitic (Lipari obsidian) glasses were measured alongside the tephra to assess analytical performance. Full details of the settings are presented in Hayward (2012).

Tephra layers were linked to known eruptions through comparison with published elemental data from TephraBase (Newton et al., 2007) with a particular focus on the Hekla-4 and Glen Garry tephra which were both expected to be found in our sites (Newton et al., 2007). Based on the recommendations in Dugmore et al. (1995), distinctive oxide ratios of FeO and TiO₂ were primarily used in the identification of Hekla 4, while CaO and MgO ratios were used for Glen Garry.

Radiocarbon dating

Macrofossils of above-ground and near surface material were located within the peat core and cleaned in preparation for radiocarbon analysis. Samples selected for ¹⁴C dating comprised *Sphagnum* austini leaves, *Molinia caerulea* rhizomes, woody twigs of *Betula* spp., stems of unidentified brown mosses and charcoal fragments. In total, 11 samples were dated from the full length of the Cross Lochs core and one sample each from the base of each of the Catanach and Bad a' Cheo cores (Table 2). Samples were dated at the Poznan Radiocarbon Laboratory (Poznan, Poland) and DirectAMS (Washington, US).

Table 2. Radiocarbonage, depth, calibrated age and 1σ calibrated age range for the AMS radiocarbon dates used in the age–depth models.

Site:	Lab no.	Mid-point depth (cm)	Material selected for dating	Radiocarbon date (BP)	Best estimate (cal BP)	1σ Calibrated age range (cal.BP)
Cross Lochs	Poz-62862	42	Charcoal	1885 ± 30	1834	1731-1890
Cross Lochs	Poz-62861	59.5	Charcoal	2405 ± 30	2426	2349-2682

<i>Cross Lochs</i>	<i>Poz-62858</i>	<i>81.5</i>	<i>Sphagnum austinii leaves</i>	<i>2600 ± 50</i>	<i>2735</i>	<i>2495-2844</i>
<i>Cross Lochs</i>	<i>Poz-62863</i>	<i>94.5</i>	<i>Charcoal</i>	<i>2805 ± 30</i>	<i>2907</i>	<i>2804-2995</i>
<i>Cross Lochs</i>	<i>D-AMS 006128</i>	<i>118.5</i>	<i>Molinia caerulea rhizome</i>	<i>3092 ± 25</i>	<i>3296</i>	<i>3234-3370</i>
<i>Cross Lochs</i>	<i>Poz-62864</i>	<i>145.5</i>	<i>Charcoal</i>	<i>3580 ± 30</i>	<i>3882</i>	<i>3777-3977</i>
<i>Cross Lochs</i>	<i>Poz-62860</i>	<i>201.5</i>	<i>Molinia caerulea Rhizome</i>	<i>5040 ± 35</i>	<i>5815</i>	<i>5664-5902</i>
<i>Cross Lochs</i>	<i>Poz-62766</i>	<i>256</i>	<i>Molinia caerulea rhizome</i>	<i>4170 ± 80</i>	<i>4694</i>	<i>4446-4862</i>
<i>Cross Lochs</i>	<i>D-AMS 006126</i>	<i>330</i>	<i>Molinia caerulea rhizome</i>	<i>8279 ± 32</i>	<i>9287</i>	<i>9136-9405</i>
<i>Cross Lochs</i>	<i>D-AMS 006127</i>	<i>312.5</i>	<i>Molinia caerulea rhizome</i>	<i>7787 ± 32</i>	<i>8568</i>	<i>8460-8632</i>
<i>Cross Lochs</i>	<i>D-AMS 006125</i>	<i>348.5</i>	<i>Betula stem</i>	<i>8567 ± 33</i>	<i>9535</i>	<i>9491-9558</i>
<i>Bad a' Cheo</i>	<i>Poz-62859</i>	<i>427.5</i>	<i>Brown moss stems</i>	<i>7830 ± 50</i>	<i>8614</i>	<i>8455-8855</i>
<i>Catanach</i>	<i>Poz-62866</i>	<i>162</i>	<i>Charcoal</i>	<i>5080 ± 35</i>	<i>5816</i>	<i>5745-5910</i>

AMS: accelerator mass spectrometry.

Age–depth models and carbon accumulation

Age–depth models were constructed using the Bayesian modelling package BACON (Blaauw and Christen, 2011), using a combination of tephra and accelerator mass spectrometry (AMS) radiocarbon dates. The calibrated age of the Hekla 4 eruption had a much lower chronological error associated with the calendar age and was therefore particularly useful in constraining the model. BACON uses prior information such as plausible accumulation rates and the law of superposition to reduce uncertainty and produce a more realistic model (Blaauw and Christen, 2011). Priors for accumulation mean, accumulation shape and memory mean were set at default values based on the compilation of Goring et al. (2012). Data on bulk density and C content were combined with the BACON age– depth models to produce reconstructions of C accumulation which incorporate temporal uncertainty.

Results

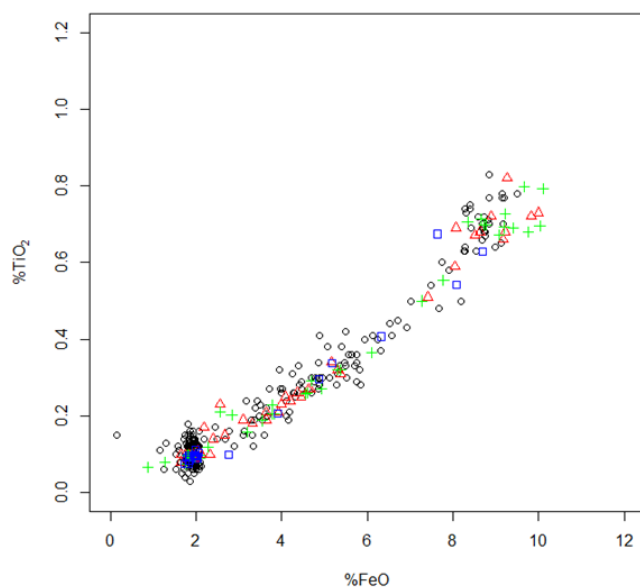


Figure 2. % TiO and FeO of reference Hekla 4 shards from Tephabase (Newton et al., 2007), displayed as black circles, compared with shards from Cross Lochs, red triangles; Catanach, green crosses; and Bad a' Cheo, blue squares.

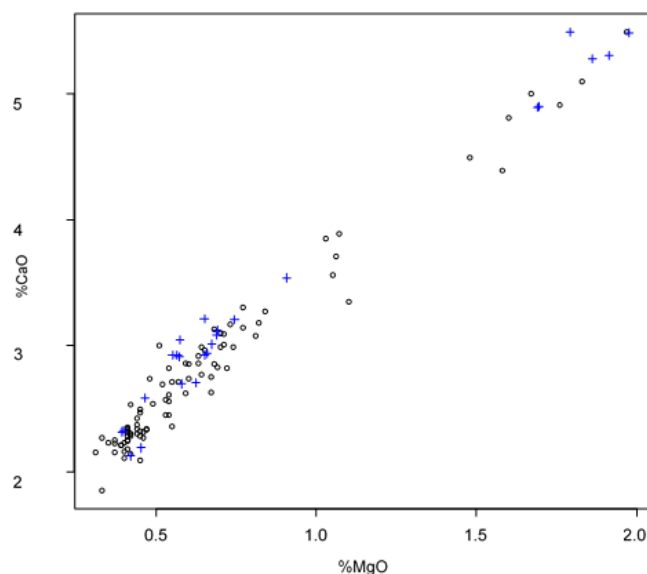


Figure 3. Calcium and magnesium oxide concentration of BADO134 shards, blue crosses, compared with reference material for the Glen Garry eruption obtained from Tephabase (Newton et al., 2007), black circles.

Tephrochronology

Four identifiable tephra layers were found: two in the Bad a' Cheo core, BADO 134.3 and BADO 200.1, and one each in Catanach and Cross Lochs cores, CATO 116.7 and CRSLO 165.6, respectively. Geochemical analyses produced results which strongly correlated with the Hekla 4 eruption (c. 4287 ± 58 cal. BP; Pilcher and Hall, 1996) for three of the tephra layers – BADO 200.1, CATO116.7 and CRSLO 165.6 (Figure 2) – and the Glen Garry eruption (c. 2176 ± 244 cal. BP; Barber et al., 2008) for the remaining layer – BADO 134.3 (Figure 3; Supplementary Material, available online). These four tephra layers were used in the age–depth models. An additional tephra layer with geochemistry strongly matching that of the Lairg A eruption was also found in analysable quantities at 2.28 m depth, in a core taken 200 m away from Bad a' Cheo within a conifer plantation (Ratcliffe, 2015). Three more potential tephra layers were detected in the Cross Lochs core, but because of the low density of shards, we were unable to correlate them to an eruption using EPMA. More details of these can be found in Ratcliffe (2015).

Radiocarbon dating

Radiocarbon dates ranged from 1885 ± 30 to 9287 ± 32 BP (Table 2) and generally had low error, with a mean uncertainty of ± 127 years in the 1σ calibrated age. All dates conformed to the law of superposition, with one exception. Poz-62766 was much younger than expected, and this date is suspected to be inaccurate. The radiocarbon laboratory noted that Poz-62766 contained less than the minimum advisable weight of C. It was included in the age–depth modelling, but the preferred model does not pass through it. Radiocarbon dating suggests peat initiation at 9491–9558 1σ cal. BP for Cross Lochs, 5745–5910 1σ cal. BP for Catanach, and 8455–8855 1σ cal. BP for Bad a' Cheo (Table 2).

Age–depth models

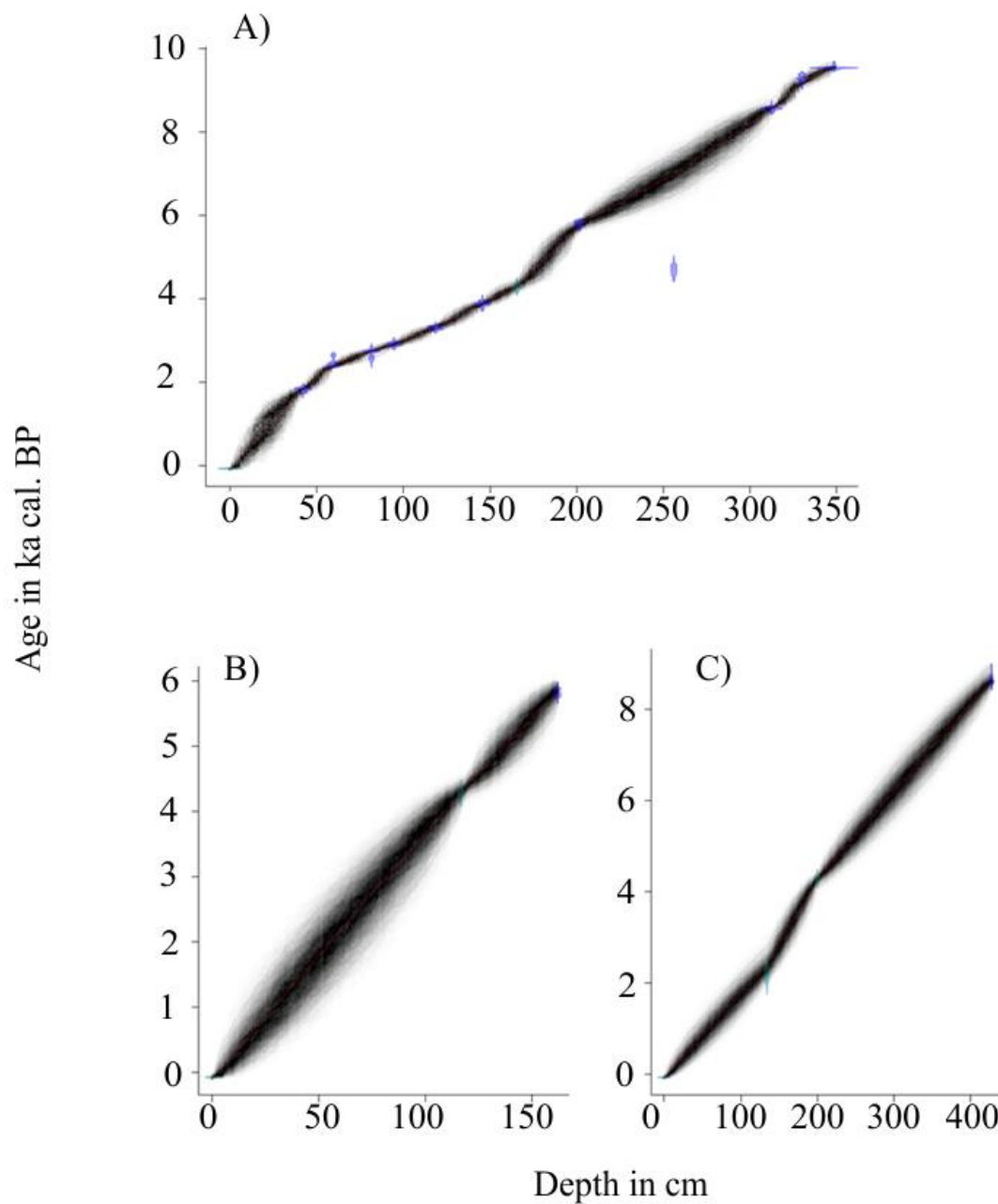


Figure 4. Age–depth models produced in BACON for (a) Cross Lochs, (b) Catanach and (c) Bad a' Cheo. Thickness of the plot represents the uncertainty in the age.

An age–depth model was produced for each site (Figure 4) to show the estimated uncertainty in the age of peat throughout the profile. The Cross Lochs core is better constrained, with less uncertainty for peat age at a given depth compared with Bad a' Cheo and Catanach. The time period from 2 to 4 ka cal. BP is perhaps the best constrained, whereas uncertainty is higher for both the last 2 ka and for the early Holocene.

Carbon accumulation

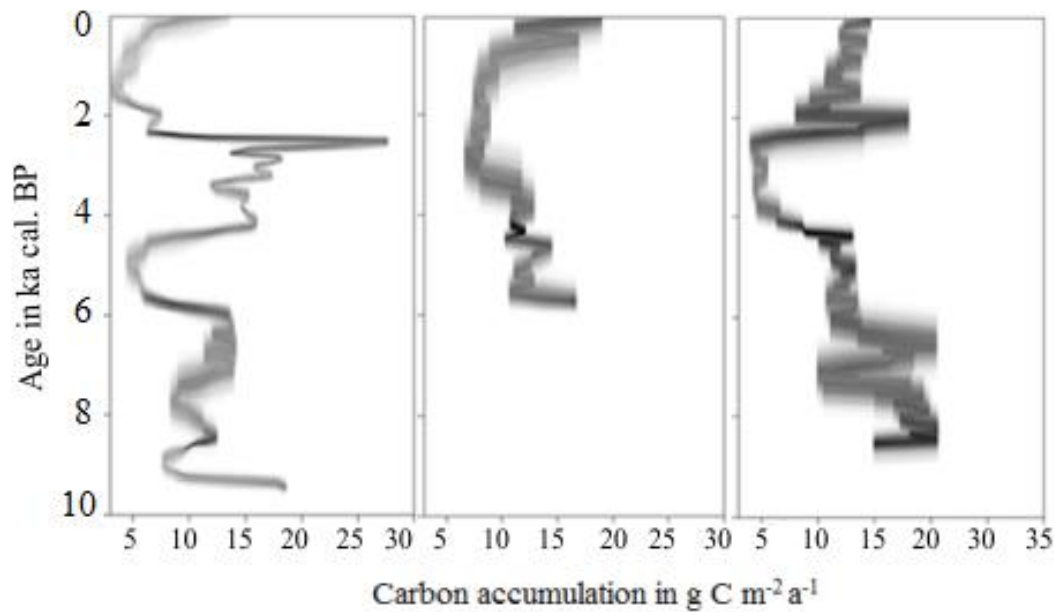


Figure 5. Long-term carbon accumulation rates over time for Cross Lochs, Catanach and Bad a' Cheo. Thickness of the plot represents the uncertainty in age.

Peat has accumulated throughout the Holocene, with no evidence for any hiatuses (Figure 5). Accumulation rates varied between 8 and 32 $\text{g C m}^{-2} \text{yr}^{-1}$. Cross Lochs had an average C accumulation rate of $15.43 \pm 5.06 \text{ g C m}^{-2} \text{yr}^{-1}$, while for Catanach it was $16.47 \pm 4.20 \text{ g C m}^{-2} \text{yr}^{-1}$. The average C accumulation rate for the Bad a' Cheo profile was $17.43 \pm 4.90 \text{ g C m}^{-2} \text{yr}^{-1}$.

At Cross Lochs, the C accumulation rate was above average in the early Holocene and decreased rapidly at c. 6030 cal. BP. Carbon accumulation began to increase again just before c. 4570 cal. BP and peaked around c. 2890 ka cal. BP before decreasing rapidly. There was then a slow increase in C accumulation up to the boundary with the acrotelm (Figure 5).

Results for the Catanach site imply that carbon accumulation was most rapid in the first 2560 years after initiation, with rates in the region of 16–20 $\text{g C m}^{-2} \text{yr}^{-1}$, followed by a decrease down to 12–15 $\text{g C m}^{-2} \text{yr}^{-1}$ which persisted until c. 940 cal. BP (Figure 5) and the transition zone to acrotelm peat.

Bad a' Cheo also had relatively higher carbon accumulation rates during the early Holocene, with a decrease around 6520 cal. BP. Carbon accumulation was fairly stable until just before c. 4 ka cal. BP when it declined and remained low until around 2 ka cal. BP. There was then a rapid increase in the average rate of carbon accumulation similar to levels recorded between c. 6 and 4 ka cal. BP (Figure 5).

Carbon accumulation rates in the Cross Lochs and Bad a' Cheo cores during the early to middle Holocene were consistently above the long-term averages for these sites, and both decreased around 6.5–6 ka cal. BP. At that time, the younger Catanach peatland commenced peat formation. Changes in C accumulation rates for the late Holocene are more contradictory, with the period of c. 4–2.5 ka cal. BP representing the highest accumulation rates for the Cross Lochs core, the lowest for Bad a' Cheo and intermediate values for Catanach. Carbon accumulation rates between 2 ka and 750 cal. yr BP for Bad a' Cheo and Catanach were close to the long-term mean, while at Cross Lochs accumulation rates were among the lowest seen since bog development was initiated. However, interpretation of the Bad a' Cheo and Catanach records is limited by the available dating points.

Discussion

Carbon accumulation and climate in peatlands of northern Scotland

LORCA for the three sites in our study was $16.44 \text{ g C m}^{-2} \text{ yr}^{-1}$, slightly lower than the value of $21.3 \text{ g C m}^{-2} \text{ yr}^{-1}$ reported for three sites in the Northwest Highlands by Anderson (2002). However, these rates are very similar to the mean rate of $18.6 \text{ g C m}^{-2} \text{ yr}^{-1}$ estimated for northern peatlands globally (Yu, 2011). Our values include C stored across the whole profile including the acrotelm, as do the majority of published values for LORCA. However, long-term peat accumulation depends on the transfer of organic material from the acrotelm to the catotelm (Wieder, 2001), and the proportion of primary production which actually reaches the catotelm is highly variable (Yu et al., 2001). This will depend on factors such as litter quality, litter turnover and acrotelm (water table) depth (Bauer, 2004). Thus, the inclusion of the acrotelm will overestimate the long-term C accumulation rate as younger peats have undergone relatively less decomposition than older peats (Clymo et al., 1998). It is difficult to predict what proportion of organic matter in the acrotelm will be transferred to the catotelm. For example, the recent rate of C accumulation (RERCA) for Scottish peats has been found to be $35\text{--}209 \text{ g C m}^{-2} \text{ yr}^{-1}$ over the last 150 years (Billett et al., 2010), which for our cores would represent approximately the top 0.1 m of the profile or the upper half of the acrotelm. It is difficult to say how much of this RERCA will be retained in the peat over a given time period without considering the individual ecohydrological properties of the peatland. In a review of several thousand peat profile measurements, RERCA was found to be poorly correlated to LORCA (Turunen, 2003).

Initiation of peat development was not uniform across sites. Peat formation at Cross Lochs and Bad a' Cheo commenced in the early Holocene, which was a period of both rapid lateral expansion and C accumulation for northern peatlands globally (Yu et al., 2009), while at Catanach peat accumulation did not occur until the middle Holocene at 5.7–5.9 ka cal. BP and coincided with a decline in tree cover and an increase in *Calluna* pollen at the regional scale between 6.8 and 4.6 ka cal. BP (dates published in Charman (1994) and calibrated here for comparative purposes using OxCal) which may be linked to bog expansion (Charman, 1992, 1994). At all three sites in this study, the peat was directly underlain by bedrock or glacial till, and no evidence of lake mud was found, indicating that paludification, rather than terrestrialsation, was the dominant process in peatland initiation.

Perhaps the most dramatic change in Holocene C accumulation rates (Figure 5) occurred at approximately 4.4 ka cal. BP. During this time, *Pinus sylvestris* colonised a large area of Scottish blanket bog in response to drying of the climate, which may have been induced by a migration of the jet stream northwards (Gear and Huntley, 1991). About four centuries later, the regional climate became wetter and colder (Anderson et al., 1998), triggering the regional extinction of *P. sylvestris* located on blanket bog (Gear and Huntley, 1991). In a nearby pollen core, the pollen assemblage shows a rise in *Empetrum nigrum* immediately prior to the sudden and short-lived peak in *P. sylvestris*, supporting the hypothesis of drier regional conditions at this time (Charman, 1990).

Only the core chronology for Cross Lochs is detailed enough at this point in the stratigraphy (Table 2) to interpret sub-millennial changes, which may explain the differing response in C accumulation seen for Catanach and Bad a' Cheo. There was a moderate increase in C accumulation at Cross Lochs during the dry period between 4.3 and 3.9 ka cal. BP followed by a much greater increase in the wet period from 3.9 to 3.3 ka cal. BP. Carbon assimilated as leaf litter is particularly sensitive to climate for a period of decades to centuries after fixation, while it is stored in the aerobic acrotelm (Frolking et al., 2014). Therefore, it is important to note that the better preservation conditions of the wet period may have resulted in better preservation of the C fixed during the preceding dry period.

These findings are in agreement with those for the same time period published in Anderson (2002), but are somewhat contradictory to when compared with other findings from later time periods. Changes in solar activity and the length of growing season have been found to be the dominant drivers of C accumulation at the centennial scale during the late Holocene (Charman et al., 2013; Mauquoy et al., 2002, 2008). However, as the response of peatland C to changes in climate and hydrology is often non-linear (Laiho, 2006; Swindles et al., 2012), fair comparisons cannot be made unless the same time period, and therefore the same climatic drivers, are being compared. Our results and those of Anderson (2002) indicate some of the most dramatic changes in Holocene peatland C accumulation have occurred in the middle Holocene, around the time of the temporary expansion of *P. sylvestris* on to blanket bog. Therefore we suggest this may be one of the most interesting periods to study environmental drivers of peatland C accumulation.

The potential utility of core scanning

A major limitation to producing more records of Holocene C accumulation is the cost of dating date peat cores at high resolution (Payne et al., 2016). Tephrochronology offers the potential for precise dates, but at the expense of time-consuming analyses. We found that core scanning was capable of rapidly locating cryptotephra. Denser layers, such as CRSLO165.6, were immediately obvious, showing up as dark bands on the x-radiograph, similar to those reported by Dugmore and Newton (1992) and producing distinguishable peaks across a range of elements. However, these were not found to be representative of the more detailed geochemistry recorded in Figures 2 and 3. Smaller layers such as BADO134.3 induced a more subtle response, with no visible band on the x-radiograph and element peaks barely visible above background levels. All peaks in the elemental data needed to be verified for the presence of tephra using optical microscopy, and many false positives were found, but the reduction in labour was still considerable. Therefore, we believe that wider adoption of core scanning may encourage the greater use of tephrochronology in peatland palaeoecological research. The core scanner also revealed several distinct cryptotephra layers in the Cross Lochs core which had shard concentrations too low to be successfully analysed. However, chronostratigraphic matching indicates that the layer located at 1.383 m might have originated from the Hekla-S/Kebister eruption, and the layer at 2.520 m from Lairg A. The presence of at least 14 identifiable cryptotephra layers in Scotland (Swindles et al., 2011) demonstrates the potential of tephrochronology for contributing to the chronology of future profile-based estimates of C accumulation.

Comparison of core-based and EC flux-based carbon accumulation rate estimates

The LORCA calculated for Cross Lochs, $15.43 \text{ g C m}^{-2} \text{ yr}^{-1}$, is much lower than that of the NECB of $99.37 \text{ g C m}^{-2} \text{ yr}^{-1}$ published in Levy and Grey (2015). Such differences between LORCA and contemporary NECB seem to be the norm rather than the exception (Table 1), although the number of sites for which both data are available is admittedly small. Lac la Biche, Moanatuatua and Moor House (Table 1) show particularly large differences in C accumulation derived from the two approaches, with NECB approximately three to six times greater than LORCA. This is despite having inter-annual flux data sets and allowing for measured, or realistic estimates, of non-CO₂ fluxes. For example, C losses through CH₄ emissions from bogs, which constitute all sites in Table 1 with the exclusion of Lac la Biche, typically do not exceed 8 g C yr^{-1} (Roulet et al., 2007). For fens, of which Lac la Biche is an example, CH₄ emissions may be higher but would not typically exceed 35 g C yr^{-1} (Bäckstrand et al., 2009). The export of DOC from intact peatlands is typically $10\text{--}20 \text{ g C m}^{-2} \text{ yr}^{-1}$ (Frolking et al., 2009) but may be as high as $25\text{--}40 \text{ g C m}^{-2} \text{ yr}^{-1}$ for drained peatlands (Billett et al., 2004; Dinsmore et al., 2010; Strack and Zuback, 2013). Consequently, non-CO₂ fluxes would need to be unrealistically high to explain the discrepancy between contemporary and long-term C balance for the three sites in Table 1 which do not include DOC and CH₄. As such, contemporary C accumulation is clearly greater than long-term C accumulation at a range of sites across the world, despite the slowdown in C accumulation which might be expected as peatland ecosystems mature (Clymo et al., 1998). Possible explanations for this may be found in the operational timescales of different drivers of peatland C dynamics (Yu, 2006b). The drivers of C accumulation over centennial to millennial timescales should not be expected to be the same as those driving inter-annual variation (Frolking et al., 2014).

For example, the flux density of photosynthetically available radiation (PAR) usually drives fluxes at daily or shorter timescales, through the impact on plant photosynthesis. While PAR is highly variable from day to day and also century to century (Mauquoy et al., 2008), inter-annual variability in PAR can be quite low (Strachan et al., 2016). As such, at the inter-annual scale, precipitation and temperature may be better predictors of C dynamics (Peichl et al., 2014; Strachan et al., 2016). This is not because precipitation and temperature are fundamentally more important to peatland C balance but because they tend to show greater variance than PAR over that interval. Similarly, variance in other drivers of peatland C accumulation, such as vegetation type, fire and low-frequency changes in climate (Frolking et al., 2014; Turetsky et al., 2002), will be close to zero over the intervals EC can practically measure, but could become a significant or even dominant source of variance over longer intervals. The environmental drivers of C dynamics in peatlands, over a given time period, will be strongly influenced by the variance in drivers that occurs over that period. Lack of variance over the timescales measured means some important drivers of the C balance simply cannot be accounted for.

Fire is known to be a particularly important component of long-term C dynamics (Pitkanen et al., 1999) and plays a prominent role in the functioning of the majority of northern peatlands (Turetsky et al., 2015). However, including

fires in the contemporary peatland C balance is impractical as they occur only intermittently. At Cross Lochs, fire has been common since the early Holocene (Charman, 1992; Robinson, 1987) and charred *Calluna* remains have been found in the surface peat not far from the EC site (Charman, 1990). A single fire event may release C accumulated over a century or more (e.g. 140 years; Pitkanen et al., 1999) and may reduce C uptake in peatlands by as much as 85% over their developmental history (Turetsky et al., 2002). This lost C, and associated peat depth, will cause an apparent slowing of the long-term C accumulation rate. Contemporary C sink strength can then be increased for up to 75 years following a fire as vegetation recovers (Harden et al., 1997; Trumbore and Harden, 1997; Ward et al., 2007; Wieder et al., 2009). Depending on the timing of measurements, this may result in a situation where C losses from fire are not recorded in the contemporary C balance but increased C sequestration after the fire is recorded. If this occurs, then the contemporary C sink would be expected to be greater than the long-term C accumulation rate.

The relationship between environmental variables and C dynamics becomes increasingly complex over longer timescales and strong relationships recorded over inter-annual timescales cannot always be assumed to stand up over longer time periods. The indirect effects of environmental drivers on peatland C dynamics will be moderated through ecohydrological feedbacks operating over many decades (Laiho, 2006; Waddington et al., 2015). These feedbacks can result in either an amplification or a dampening of the influence of environmental conditions on peatland C dynamics (Laiho, 2006; Swindles et al., 2012; Waddington et al., 2015). For example, feedbacks between water table, decay and peat hydraulic conductivity may cause decay rates to be relatively insensitive to changes in precipitation over long periods of time (Swindles et al., 2012; Waddington et al., 2015). Yet alternatively, positive feedbacks may enhance the impact of changes in precipitation on C balance through changes in vegetation, modification of transpiration rates and further lowering of the water table (Waddington et al., 2015). Thus, thresholds of peatland ecohydrological response, that is, whether negative or positive feedbacks will be dominant and over what timescale, are important considerations to be made when assessing the environmental drivers of peatland C balance (Limpens et al., 2008).

Carbon sequestration rates close to $100 \text{ g C m}^{-2} \text{ yr}^{-1}$ in ombrotrophic bogs are likely to be unsustainable in the long term, as values of C accumulation inferred from profile measurements rarely come close to $100 \text{ g C m}^{-2} \text{ yr}^{-1}$ and have only ever been recorded for peatlands in the early stages of initiation (Page et al., 2004; Pendea and Chmura, 2012) or for fen peats in response to rapid changes in hydrology (Yu et al., 2003). Litter inputs into peatlands typically undergo comparatively rapid decay in the acrotelm for a period of decades to centuries (Malmer and Wallén, 2004) before passing into the relatively stable catotelm. The portion of the photosynthetically fixed C which reaches the catotelm will depend on the amount of decay this material undergoes. This is controlled by factors such as mean position and variability of the water table depth, along with temperature and the properties of the litter inputs (Bauer, 2004; Clymo et al., 1998). Short-term increases in C accumulation can actually represent changes in acrotelm thickness, rather than any change in input to the relatively stable catotelm (Belyea and Clymo, 2001). This could be expected in bogs where vascular plant cover is increasing, resulting in higher, but more easily decomposable, litter inputs (Malmer et al., 2005; Waddington et al., 2015). For example, the primary production in sedge-dominated fens is usually much higher than in *Sphagnum* bogs, yet C accumulation is on average lower for fen peats because of differences in litter quality (Rydin et al., 2006; Turunen, 2003). The stability of C added to the acrotelm, and the portion of it which ultimately reaches the long-term store in the catotelm, should be considered when assessing the sink strength of a peatland based on the contemporary NECB.

It has been hypothesised that environmental change has caused an increase in NECB, relative to Holocene C accumulation rates, across northern peatlands (Yu, 2012), and this could be the case at Cross Lochs. The specific drivers of this change could include lengthening of the growing season, increased nitrogen deposition and CO₂ enrichment, all of which have been predicted to cause an increase in peatland C accumulation rates (Charman et al., 2013). Nitrogen deposition for Forsinard has been estimated at $6.3 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, a value which is lower than much of the UK but is high enough to impact on many peatland vegetation communities (Payne, 2014). The growing season has increased by >5 weeks relative to 1961 (Sniffer, 2014). CO₂ enrichment has been demonstrated to increase primary production in forests by as much as 25% (DeLucia et al., 1999), while the effects of CO₂ enrichment on nutrient-poor peatlands appear to be small (Hoosbeek et al., 2001). However, the combined effects of increased N deposition and CO₂ enrichment have seldom been explored (Siegenthaler et al., 2010). Modelling of peatland C processes is required to 'bridge the gap' between NECB and LORCA (Bauer, 2004) and can be used to forecast the fate of recently fixed C. This has proved to be challenging thus far because of the numerous interacting processes

and feedbacks involved in peatland ecohydrology (Waddington et al., 2015), and the lack of good palaeo and contemporary data on C accumulation and ecological parameters at the site level, such as decay and productivity rates. Locating palaeoecological work at flux sites and conversely locating new flux sites in peatlands with a well-studied palaeoecology, for example those outlined in Payne et al. (2016), would facilitate better modelling in the future.

Conclusion

Large discrepancies exist between contemporary and long-term C accumulation rates across a number of peatlands globally, including in our blanket bog site, Cross Lochs, in the north of Scotland. Long-term C accumulation rates provide a measure for C which has been retained in the deeper catotelm peat but provide a poor measure of current C accumulation rates. NECB provides a measure of a peatland's current C balance; however, we argue that when considered in isolation, NECB may provide a poor indicator of peatland ecosystem C dynamics over intermediate and longer timescales. The context provided by long-term C accumulation rates, published here and in other studies, would suggest that contemporary C accumulation rates at or greater than 100 g C yr^{-1} are not sustainable in the medium to long term in ombrotrophic bogs. While productivity dominates the variance in peatland C accumulation over short timescales, this becomes progressively less so over longer time periods. C fixed through primary production will be most vulnerable to fire and microbial decay over the following period of acrotelm residence time, typically a period of decades to centuries. Thus, decay and disturbance become more important when considering progressively longer timescales.

Changes in vegetation communities over the period of acrotelm residence preceding flux measurements may result in contemporary CO₂ fluxes which compare the primary production of the contemporary vegetation community with the heterotrophic respiration of litter dominated by former communities. For instance, a peatland which has seen a recent shift from *Sphagnum* towards vascular species may have higher rates of primary productivity associated with vascular plants. However, low rates of heterotrophic respiration associated with *Sphagnum* litter, which may still be the dominant source of heterotrophic respiration, may be retained. Such a site would show strong C sink activity for a temporary period, until the acrotelm litter composition changes to become representative of the current community.

Thus, when NECB is used as an assessment of C balance, and especially when extrapolating to the regional scale, peatland C flux measurements should be considered together with how representative the current vegetation community is of the downcore acrotelm litter. Equally important when extrapolating data over longer timescales is the amount of decay that recently fixed C is likely to undergo before it reaches the relatively stable catotelm. While site productivity derived from contemporary fluxes is relatively straightforward to interpret, heterotrophic respiration will be strongly influenced by the palaeoecology of the individual site; therefore, we recommend that future studies of peatland C balance should combine contemporary and palaeo approaches. This would have the advantage of producing data with which to parameterise and validate site-level models of C accumulation, which are ultimately needed to better predict future peatland C dynamics.

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